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(54) **Components and catalysts for the polymerization of olefins.**

(57) Catalysts for the polymerization of alpha-olefins which comprise the reaction product of:

a) an Al-alkyl compound;
b) a silicon compound containing at least a Si-OR or Si-OCOR or Si-NR_2 bond, R being a hydrocarbyl radical;
c) a solid comprising as essential support, a Mg dihalide in active form and supported therein a Ti halide or a halo-Ti-alcoholate and a particular type of electron donor compound.

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DESCRIPTION

The present invention refers to new supported components of catalysts for the polymerization of CH_2=CHR olefins wherein R is an alkyl radical with 1 to 4 carbon atoms, or an aryl radical, and mixtures of said olefins with ethylene and the catalysts obtained from said components.

The supported highly active and highly stereospecific catalysts up to now known for the polymerization of propylene and higher olefins, are obtained by the reaction of an Al-alkyl compound partially complexed with an electron donor compound (outside donor) with a solid component comprising a Ti compound and an electron-donor compound (inside donor) supported on a Mg-halide in active form.

Examples of such catalysts have been described in British Patent No. 1,559,194 and Belgian Patent No. 868,682.

Outside donor consisting of silicon compounds containing Si-O-C bonds have been also described (Japanese patent application Sho 79/94590 and Sho 80/36203). Among the various and numerous inside donors also com-

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pounds as methylmethacrylate and ethyl pivalate have been cited. However in all the prior art catalysts in which a silicon compound containing Si-O-C bonds is used as outside donor, esters of benzoic acid and derivatives thereof are used as inside donor.

The performance of the above catalysts, expressed in terms of activity and stereospecificity is not different from the performance of the catalysts in which ethyl benzoate and similar esters of benzoic acid are used as outside donor.

It has now unexpectedly been found that it is possible to increase the activity and stereospecificity of the prior art supported catalysts comprising as outside donor a silicon compound containing Si-O-C bonds by using as inside donor an ester having a particular structure.

The catalysts of this invention comprise the product of reaction between the following components:

a) an Al-trialkyl or an Al-alkyl compound containing 2 or more aluminum atoms linked to each other through oxygen or nitrogen atoms or through SO_4 or SO_3 groups;

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b) a silicon compound containing one or more Si-OR, Si-OCOR or $Si-NR_2$ bonds (R being a hydrocarbyl radical);

c) a solid comprising, as essential support, an anhydrous Mg-dihalide present in active form, and supported on said dihalide a Ti-halide or a Ti-haloalcoholate and an electron-donor compound selected from the following groups of compounds:

1) Mono and diesters of aromatic bicarboxyl acids having the COOH groups in orto position wherein the R hydrocarbyl radicals of the COOR groups contain less than 3 carbon atoms and at least one of said R radicals contains 2 carbon atoms.

2) Esters of saturated and unsaturated carboxylic acids of formula RCOOR' wherein the R hydrocarbyl radical is either a saturated or unsaturated branched radical containing from 3 to 20 carbon atoms or an arylalkyl radical with 7 to 20 carbon atoms or an aryl radical with 3 to 20 carbon atoms linked to the esteric carbonyl group directly or through a methylene group and in which R' is a hydrocarbyl radical with less than 3 carbon atoms.

Compounds representative which are also the preferred are the following: diethylphthalate, methylethylphthalate, diethyl-

-2,3-naphthalendicarboxylate, methyl and ethyl pivalate, methyl and ethyl methacrylate.

As indicated, the esters of the polycarboxylic acids can contain beside the ester groups also unexterified COOH groups.

In preparing component c) the esters are contacted with the active Mg dihalide or the precursors of said dihalides as preformed compounds or the esters can be formed in situ by means of known reactions as for instance by esterification between an alcohol or an alcoholate and an aryl halide or between an anhydride or an emiester of a polycarboxylic acid with an alcohol or by transesterification. The esters can also be used in mixture with other known inside donors.

The active anhydrous Mg dihalides forming the essential support of component c) are the Mg dihalides showing in the X-ray powder spectrum of component c) a broadening of at least 30% of the most intense diffraction line which appears in the powder spectrum of the corresponding dihalide having 1 m^2/g of surface area or are the Mg dihalides showing a X-ray powder spectrum in which said most intense diffraction line is replaced by a halo with the intensity peak shifted with respect to the interplanar

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distance of the most intense line and/or are the Mg dihalides having a surface area greater than 3 m^2/g.

The measurement of the surface area of the Mg dihalides is made on component c) after treatment with boiling $TiCl_4$ for 2 hours. The found value is considered as surface area of the Mg dihalide.
Very active forms of Mg dihalides are those showing a X-ray powder spectrum in which the most intense diffraction line appearing in the spectrum of the corresponding halide having 1 m^2/g of surface area is decreased in relative intensity and broadened to form a halo or are those in which said most intense line is replaced by a halo having its intensity peak shifted with respect to the interplanar distance of the most intense line. Generally the surface area of the above forms is higher than 30-40 m^2/g and is comprised in particular between 100-300 m^2/g.

Active forms are also those deriving from the above forms by heat-treatment in inert hydrocarbon solvents and showing in the X-ray spectrum sharp diffraction lines in place of the halos.

The sharp, most intense line of these forms shows a broadening of at least 30% with respect to the correspon

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ding line of the Mg dihalide having 1 m^2/g of surface area. Preferred Mg dihalides are Mg dichloride and Mg dibromide. The content in water of the dihalides is generally less than 1% by weight.

For Ti halides or Ti haloalcoholates and esters supported on the active Mg dihalide is meant the above compounds which may be chemically or physically fixed on the support, not extractable from component c) by treatment of the same with boiling 1,2-dichloroethane for 2 hours .

Components a), b) and c) are made to react each other in any order; preferably, however, components a) and b) are premixed before being contacted with component c).

Component c) may be premixed with either component a) and/or b). The pre-mixing of a) and b) is conducted at temperatures comprised, usually, between room temperature and the temperature used in the polymerization process.

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The pre-reaction of c) and b) may be carried out also at higher temperatures. Compound b) may be also incorporated and made to react with component c) itself. Component b) is made to react in a molar ratio with respect to the halogenated Ti compound supported on component c) of at least 1 and in a molar ratio with respect the Al-alkyl compound used as component a) of less than 20 and preferably comprised between 0.05 to 0.3.

In component c) the molar ratio between the Mg dihalide and the halogenated Ti compound supported therein is comprised between 1 and 500 and the molar ratio between said halogenated Ti compound and the electron-donor supported on the Mg dihalide is comprised between 0.1 and 50. The silicon compounds set forth in b) include compounds of general formula:

$$R_mSiY_nX_p$$

wherein:

R is an alkyl, alkenyl, aryl, arylalkyl, cycloalkyl radical with from 1 to 20 carbon atoms;

Y is a $-OR'$, $-OCOR'$, $-NR_2'$ wherein R', either equal to or different from R, has the same meaning as R;

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X is either a halogen or hydrogen atom or a -OCOR", $-NR_2$" group wherein R", either equal to or different from R', has the same meaning as R';

m, n and p are numbers comprised respectively between: m between 0 and 3, n between 1 and 4 and p between 0 and 1; and m+n+p is equal to 4.

Other silicon compounds that may be used are compounds in which two or more silicon atoms are bound to each other through oxygen or nitrogen atoms.

Examples of these compounds are hexaethoxydisiloxane, simmetrical diphenyltetraethoxydisiloxane

$$(C_2H_5O)_2-\underset{\displaystyle C_6H_5}{\underset{|}{Si}}-O-CH_2-CH_2-O-\underset{\displaystyle C_6H_5}{\underset{|}{Si}}-(OC_2H_5)_2$$

Preferred silicon compounds are: phenylalkoxysilanes as phenyltriethoxy or trimethoxysilane, diphenyldimethoxy and diethoxysilane, monochlorophenyldiethoxysilane; alkylalkoxysilanes as ethyltriethoxysilane, ethyltriisopropoxysilane.

Examples of other suitable compounds are: chlorotrie-

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tnoxysilane, acetoxytriethoxysilane, vinyltriethoxysilane, butyltriethoxysilane, triphenylmonoethoxysilane, phenyltricycloethoxysilane, phenyldiethoxydiethylaminosilane, tetraphenoxysilane or tetralkoxysilanes as tetramethoxysilane.

* In the catalysts of the invention the silicon compound is present in a combined form in the solid product of the reaction between the various catalyst- forming components, in a molar ratio between the silicon compound and the halogenated Ti compound greater than 0.05 and generally comprised between 0.1 and 5.

* The silicon compound can be also formed in situ by reaction for instance of a halogenated silicon compound as $SiCl_4$ with an alcohol or an alcoholate of Mg or Al.

The Al-alkyl compounds forming component a) includes Al-trialkyls as for instance Al-triethyl, Al-triisobutyl, Al-triisopropyl and compounds containing two or more Al atoms linked to each other through etero-atoms as:

$$(C_2H_5)_2Al{-}O{-}Al(C_2H_5)_2, \qquad (C_2H_5)_2Al{-}\underset{\substack{|\\ C_6H_5}}{N}{-}Al(C_2H_5)_2,$$

$$(C_2H_5)_2Al{-}O{-}\overset{\substack{O\\ \|}}{\underset{\substack{\|\\ O}}{S}}{-}O{-}Al(C_2H_5)_2.$$

As indicated Al-alkyl compounds in which Al atoms are linked through groups as SO_4 or SO_3 are also suitable.

The Al-alkyl compounds may be used in mixture with Al-alkyl halides as $AlEt_2Cl$.

Component c) is prepared according to known methods. One of these methods consists in co-milling the Mg halide and the electron-donor compound of this invention until the appearance in the X-ray spectrum of the milled product of the modifications above set forth for the spectrum of the Mg dihalide and thereafter reacting the milled product with the Ti-compound.

Preparations of this type are described in British Patent No. 1,559,194.

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Similar preparations are described in U.S. Patents Nos. 4,107,413, 4,107,414 and 4,107,415.

Another method consists in reacting the adduct of a Mg halide with an alcohol, with a Ti compound in the pre sence of an electron-donor compound not containing active hydrogen atoms. This method is described in Belgian Patent No. 868,682.

According to another method, which is described in published German application 3,022,738, the adduct between the Mg dihalide and the alcohol is reacted in liquid form with the halogenated Ti compound and the electron-donor compound.

Further methods are described in published German application 2,924,029, U.S. Patent 4,220,554 as well as in Italian Patent Application No. 27.261/79.

Another method consists in co-milling the Mg dihalide, the halogenated Ti compound and the electron-donor compound until activation of the Mg dihalide and in treat ing a suspension of the milled product in a halogenated hydrocarbon as 1,2-dichloroethane, chlorobenzene, methylene chloride, hexachloroethane.

The treatment is carried out at temperatures comprised

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between 40°C and the boiling point of the halogenated hydrocarbon for a time ranging in general from 1 to 4 hours.

According to another method a porous support like SiO_2 or Al_2O_3, having a low content of OH groups (preferably less than 1% by weight) is impregnated with a liquid adduct between the Mg dihalide and an alcohol; the support is then treated with an excess of $TiCl_4$ containing dissolved the electron-donor compound according to the procedure described for instance in German patent application 3,022,738 or Belgian patent 868,682.

In all the above methods the final product contains a Mg dihalide, present in the active form as set forth here above.

Other known methods which lead to the formation of Mg dihalide in active form or to Ti- containing Mg dihalide supported components, in which the dihalide is present in active form, are based on the following reactions:

- reaction of a Grignard reagent or a Mg R_2 compound (R being a hydrocarbyl radical) or complexes of said Mg R_2 compounds with Al-trialkyls, with haloge-

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nating agents as AlX_3 or $Al\ R_mX_n$ compounds (X is halogen, R is a hydrocarbyl m+n = 3), $SiCl_4$ or $HSiCl_3$;

- reaction of a Grignard reagent with a silanol or polysiloxane, H_2O or with an alcohol and further reaction with a halogenating agent or with $TiCl_4$;
- reaction of Mg with an alcohol and a halogenidric acid or of Mg with a hydrocarbyl halide and an alcohol;
- reaction of MgO with Cl_2 or $AlCl_3$;
- reaction of $MgX_2.nH_2O$ (X = halogen) with a halogenating agent or $TiCl_4$;
- reaction of Mg mono or dialcoholates or Mg carboxylates with a nalogenating agent.

The Ti-halides or Ti-halogenalcoholates, include in particular the Ti-tetrahalides, Ti-trihalides and Ti--trihalogenalcoholates. Preferred compounds are: $TiCl_4$, $TiBr_4$, 2,6-dimethylphenoxytrichlorotitanium.

The Ti-trihalides are obtained according to known methods, for instance by reduction of $TiCl_4$ with Al or a metallorganic Al compound or with hydrogen.

In case of the Ti-trihalides it may be convenient for the purpose of improving the performance of the ca-

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talysts to carry out an oxidization, even if partial, of the titanium, either during or after the preparation of component c).

To this purpose there may be used halogens, iodine halides.

Preferred catalysts are those in which: component c) is obtained from $MgCl_2$, $TiCl_4$ and diethyl phthalates, methyl and ethyl pivalates and in which component b) is phenyl or ethyltrietoxysilane or diphenyldimethoxy or diethoxysilane.

Component a) is an Al-trialkyl as Al-triethyl or Al-triisobutyl.

Component c) is prepared according the methods described in Brit. Pat. No. 1,559,194, Belgian patent No. 868,682, published German application No. 2,924,029, U.S. Patent 4,220,554, Italian Pat. Appln. 27,261/79 or published German application 3,022,738.

The preferred method of preparing component c) includes also the co-milling of $MgCl_2$, $TiCl_4$ and the ester and in treating the milled product with a halogenated hydrocarbon as 1,2-dichloroethane.

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The catalysts according to the invention are used to polymerize the alpha-olefins according to known methods that is, in carrying out the polymerization in a liquid phase, either in the presence or absence of an inert hydrocarbon solvent, or in gas phase or also by combining, for instance, a liquid phase polymerization step with a step in gas phase.

In general the temperature is comprised between 40° and 160°C, but preferably between 60° and 90°C, operating either at atmospheric or at greater than atmospheric pressure.

As a molecular weight regulator hydrogen or other regulators of a known type are used.

The catalysts are used particularly suitable in polymerizing propylene, butene-1, styrene, 4-methylpentene. The catalysts may also be used according known methods to polymerize mixtures of propylene and ethylene to form modified polypropylenes having better shock-resistance at low temperatures (the so called block copolymers of propylene and ethylene) or to obtain random crystalline copolymers of propylene with minor proportions of ethylene.

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The following examples are given for merely illustra tive purpose and are not intended to be in any way limiting the scope of the invention.

EXAMPLES 1 - 2

Into a stainless steel autoclave having a total volume of 3 l, equipped with a magnetical stirrer and a thermocouple heat-stabilized at 60°C and kept under pressure by a nitrogen atmosphere, there were introduced 1000 ml of a suspension in degassed and anhydrous n-heptane containing 5 mols of triethylaluminum, the phenyltriethoxysilane (PES) and a solid catalytic component prepared according to example 1 of Italian Pat. Appln. 27.261/79, but using, instead of ethylbenzoate, the esters listed in Table I, while propylene was also fed in. The catalytic components thus prepared showed X-ray powder spectra in which the most intense diffraction line appearing in the spectrum of $MgCl_2$ having 1 m^2/g of surface area is decreased in relative intensity and broadened to form a halo.

After closing the autoclave, hydrogen was introduced up to a pressure of 0,2 atmospheres, the temperature was brought to 70°C and simultaneously, propylene was intro-

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duced up to a total pressure of 7 atmospheres.
During the polymerization the pressure was kept constant by continuous feeding of the monomer. After 4 hours, the polymerization was stopped by quick cooling and degassing of the polymeric slurry. The polymer was separated from the solvent by filtering and was dried in a hot nitrogen flow at 70°C. The quantity of polymer dissolved in the filtrate was thereupon isolated, weighed and summed to the polymer soluble in boiling n-heptane, for the calculation of the isotacticity index (II).
The quantity of catalytic component used and the content of Ti in said component, the molar ratio of the phenyltrietoxysilane with respect to the triethylaluminium, the yield in polymer with respect to the introduced catalytic component, the isotacticity index (I.I.), the surface area of the solid catalytic component and the inherent viscosity determined in tetralin at 135°C, have all been reported in Table I.

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EXAMPLE 3

Example 1 was repeated but using a solid catalytic compon ent prepared as follows.

Anhydrous $MgCl_2$, an ester, listed in Table II, and $TiCl_4$ in molar ratio of 1:1 with respect to the ester, was co-ground in a vibrating mill of the type VIBRATOM manufactured by N.V. TEMA'S, Gravenhage (Holland), having a total volume of one liter and containing 3 kg of stainless steel balls of 16 mm diameter.

A filling coefficient equal to 100 g/g of total volume (vacuum) was used. The interior temperature of the mill was 25°C, and the grinding time was of 72 hours.

Charging of the mill, the grinding and discharging of the mill occurred in a nitrogen atmosphere.

10 g of the co-ground product was contacted with 100 ml of 1,2-dichloroethane at 80°C for 2 hours.

After this period, 1,2-dichloroethane was removed by filtration at 80°C and the residual solid product was repeatedly washed with n-heptane at room temperature till the disappearance of the chlorine ions from the filtrate and

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then was kept in heptanic suspension.

The catalytic components thus prepared showed a X-ray powder spectrum in which the most intense diffraction line appearing in the spectrum of $MgCl_2$ having 1 m^2/g of surface area was decreased in relative intensity and broadened to form a halo.

The ester, the characteristics of the solid catalytic component, and the results of polymerization test have been reported in Table II.

EXAMPLE 4

Example 1 was repeated but using a solid catalytic component prepared according to Example 3 of Italian Patent Appln. No. 26,908 A/78.

A solid adduct $MgCl_2 \cdot 3\ C_2H_5OH$ in the form of spherical particles were slowly added in a suspension of an adduct $TiCl_4$-ester using molar ratios Mg/ester of 6 and $TiCl_4/C_2H_5OH$ of 12.

The whole was then heated at 100°C, kept at said temperature for 2 hours and then filtered at 100°C. The resulting solid product was treated with 110 ml of $TiCl_4$ at 120°C for 2 hours. After this period, $TiCl_4$ was removed by filtration and the solid was then washed with n-heptane

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at temperatures decreasing from 90°C to room temperature until the chlorine ion disappeared and then kept in heptanic solution.

The catalytic component thus prepared showed the same X-ray spectrum of the catalytic component of Example 1.

The ester , the characteristics of the solid catalytic component and the results of the polymerization tests have been reported in Table I.

Comparative EXAMPLES 1 and 2

Example 1 was repeated but using the solid catalytic component prepared according to example 1 of Italian Pat. Appl. No. 27,261/79. The X-ray powder spectrum was similar to that of catalytic component of Example 1.

The results of the polymerization tests have been reported in Table I.

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Comparative EXAMPLE 3

Example 4 was repeated but using a solid catalytic compo nent prepared according to Example 3 of Italian Pat. Appl. 26,908 A/78. The X-ray spectrum of that catalytic component was similar to those of Examples 1-2. The charac- teristics of the solid product and the results of the po- lymerization tests have been reported in Table I.

TABLE I

Example No.	Solid catalytic component			Polymerization				
	Ester	$\frac{MgCl_2}{ester}$ grinding mols/mols	Ti content of solid component % by weight	$\frac{Al(C_2H_5)_3}{PES}$ mols/mols	Catalyst mg	Yield $\frac{g\ polymer}{g\ catalyst\ component}$	I.I. %	η in h dl/g
1	diethylphthalate	14	2.3	20	50	7,800	93.3	1.4
2	ethylmethacrylate	7	2.9	10	47	7,000	90.7	1.3
3	ethylbenzoylacetate	7	2.2	10	43	4,900	95.4	1.2
4	monoethylphthalate	6	2.8	20	26	6,000	96.9	1.3
mp. 1	ethylbenzoate	7	2.0	10	46	6,000	90,6	1.4
mp. 2	ethylbenzoate	7	2.0	5	47	4,000	92.7	1.6
mp. 3	ethylbenzoate		3.8	3	45	4,500	94	1.5

CLAIMS

1) A solid component to be used in combination with an Al-Alkyl compound and a silicon compound containing one or more Si-OR, Si-OCOR and Si-NR_2 bonds (R being a hydrocarbyl radical) to form catalysts for the polymerization of alpha olefins comprising an anhydrous Mg dihalide in active form, as essential support, and supported on said Mg dihalide a Ti-halide or Ti-haloalcoholate and an electron-donor compound selected from the following groups of compounds:

1.1 Mono and diesters of aromatic bicarboxylic acids having the COOH groups in ortho position, wherein the R hydrocarbyl radicals of the COOR groups contain less than 3 carbon atoms and at least one of said radicals contains 2 carbon atoms.

1.2 Esters of saturated and unsaturated carboxylic acids of formula RCOOR' wherein the R hydrocarbyl radical is either a saturated or unsaturated branched radical containing from 3 to 20 carbon atoms or an arylalkyl radical with 7 to 20 carbon atoms or an aryl radical with 3 to 20 carbon atoms and in which the R' is a hydrocarbyl radical with less than 3 carbon atoms.

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2) A solid component as defined in claim 1) in which the Mg dihalide is Mg dichloride and Mg dibromide, the Ti halide is a Ti-tetrahalide and the electron donor compound is diethylphthalate, methyl and ethylpivalate, methyl and ethyl methacrylate.

3) Catalysts for the polymerization of alpha olefins comprising the product of reaction of the following components:

a) an Al-trialkyl or an Al-alkyl compound containing 2 or more Al atoms linked to each other through an oxygen or nitrogen atom or through SO_4 or SO_3 groups;

b) a silicon compound containing one or more Si-OR, SiOCOR or Si-NR_2 bond, R being a hydrocarbyl radical;

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c) a solid component as defined in claims 1) to 3).

4) Catalysts as defined in claim 3) in which the silicon compound of component b) is a phenyl trialkoxysilane or a diphenyldialkoxysilane or an alkyl di- or trialkoxysilane.

5) Catalysts as defined in claim 4) in which component c) is the solid component as defined in claim 2).

6) Process for the polymerization of alpha olefins $CH_2 = CHR$ in which R is an alkyl radical with 1 to 4 C or an aryl radical and mixtures of said olefins with ethylene, characterized in that the polymerization process is carried out in liquid phase in presence or not of an inert hydrocarbon solvent or in gas phase in presence of a catalyst as defined in claims 3) to 5).

7) Polymers of alpha olefins obtained with the process of claim 6).

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